The Crystal Structure of Sulfur Dioxide

The Crystal Structure of Sulfur Dioxide*

Tadashi SUGAWARA and Eizô KANDA

The Research Institute for Iron, Steel and Other Metals

(Received January 5, 1950)

Synopsis

The crystal structure of sulfur dioxide was found by the x-ray powder method to have an orthorhombic unit of structure of dimensions: a=6.03Å, b=5.94Å, c=6.08Å at 95°K., containing four molecules. The probable space group was C_{2v}^{17}-Aba. By the method of trial and error, the atomic coordinates were determined as follows:

4s: (000), $(0\frac{1}{2}\frac{1}{2})+$ 00z; $\frac{1}{2}\frac{1}{2}$z with $z_s=0$;

8o: (000), $(0\frac{1}{2}\frac{1}{2})+$ xyz; $\bar{x}\bar{y}z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$ with $x_o=0.151$, $y_o=0.141$, $z_o=0.117$.

The resulting structure has a marked feature, i. e., all the molecules orientate in one direction (c-axis). On this point, the relations between this structure and physical properties were discussed. The pairing of molecules in the sulfur dioxide crystal proposed by Giauque was not consistent with our structure.

I. Introduction

The x-ray investigations on the crystal structure of condensed gases has accounted for the principles of constructing crystals whose components are simple molecules.

Most of workers have employed powder methods and succeeded in determining the crystal structure of rare gases, typical diatomic molecular gases such as nitrogen, oxygen, carbon monoxide etc., and some polyatomic molecular gases such as carbon dioxide, methane, carbonyl sulfide etc. The shape of these molecules and their crystal structure are relatively simple.

For solidified gases which crystallize in the rhombic system or in a system of lower symmetry, one can not determine the crystal structure uniquely by the powder method. For this purpose, single crystal x-ray technics at low temperatures were investigated by several authors. Ruhemann(1) constructed a simple rotation photograph camera for low temperatures, but his method was applicable only for crystals of high symmetry. Later Keesom and Taconis(2) deviced a low temperature x-ray goniometer for solidified gases. Their apparatus was too complicate in mechanism to be used generally for the determination of crystal structure. Thus single crystal x-ray methods at low temperatures is not

* The 560th report of the Research Institute for Iron, Steel and Other Metals.

(1) M. Ruhemann, Z. f. Phys., 76 (1932), 368.

(2) W. H. Keesom and K. W. Taconis, Physica, 2 (1935), 463; ibid 3 (1936), 237.

satisfactory at this stage.

On the other hand, some new devices for indexing powder photographs have been suggested. Hesse[3] reported a method of indexing photographs of the hexagonal, tetragonal and orthorhombic crystals, and Lipson[4] a method of indexing photographs of orthorhombic crystals. While, Ito[5] has proposed a general method of indexing powder photographs and by his method any powder photographs can be interpretted by the true lattice. Accordingly, the structure analysis of the crystals having low symmetry has become possible by powder photographs only and by these methods some progress will be expected in the field of the low temperature x-ray crystallography. Therefore we tried to determine the crystal structure of sulfur dioxide from the powder photograph keeping clear of the difficulty of single crystal method at low temperatures.

Sulfur dioxide crystallizes at 197.64°K and its structure is unknown, though that of the dioxide of selenium or tellurium belonging to the same group in the periodic table as sulfur has been well analysed[6],[7]. The molecular structure of sulfur dioxide has been determined by the electron diffraction of the gas[8],[9],[10].

Giauque and Stephenson[11] measured the heat capacities of the substance at the temperatures between 15°K and room temperature. According to their results, no phase change exists in that temperature range, and the zero point entropy is zero. This fact suggests that sulfur dioxide has the crystal of relatively lower symmetry even at very low temperatures.

Recently, Giauque[12] proposed that in the crystal two sulfur dioxide molecules paired at right angles forming a spherically symmetric group so as to explain the anomalous thermal expansion of the crystal observed in his heat capacity measurements.

In the following, we utilize these results for the determination of the space group and the atomic coordinates.

II. Method and Apparatus

The Material. Sulfur dioxide was prepared by the action of concentrated sulfuric acid on sodium sulfite. The evolved gas was bubbled through water to remove sulfur trioxide, and then passed through tubes containing calcium chloride and phosphorus pentoxide to remove water vapor. The gas was then liquefied in a trap and distilled several times, generous fractions being discarded

(3) Hesse, Act. Cryst., 1 (1948), 200.
(4) H. Lipson, Act. Cryst., 2(1949), 43.
(5) T. Ito, Nature, 164(1949), 755
(6) J. D. McCoulough, J. Am. Chem. Soc., 59(1937), 789.
(7) M. Goldschmidt, Skrift. Norske Vid.-Akad. Mat.-Nat. Klasse, 1926, No. 1.
(8) R. Weirl, Phys. Z., 31(1930), 1028.
(9) P. C. Cross and L.O. Brockway, J. Chem. Phys., 3 (1935), 821.
(10) V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc., 62 (1940), 1270.
(11) W. F. Giauque and C. C. Stephenson, J. Am. Chem. Soc., 60 (1938), 1389.
(12) W. F. Giauque and W. M. Jones, J. Am. Chem. Soc., 70 (1948), 120.

at the begining and the end of each distillation. Finally the sulfur dioxide was solidified by cooling with liquid air and pumped by means of a oil diffusion pump. This procedure was the same as used by Giauque[11] in his heat capacity measurements, and the purity of the material was satisfactory for structure analysis.

Low temperature x-ray camera. This was constructed for the low temperature powder photographs of condensed gases. The principle is the same as that of Vegard[13], or Günter, Holm and Strunz[14].

Details of the camera are illustrated in Fig. 1. The main parts are: A–the inner Dewar's container for liquid air or liquid hydrogen, B–the outer Dewar's container for liquid air, these are made of thin plates of German silver, C–the copper rod, D–the metal wire on which the material condenses, E–the copper-constantan theromccouple, F and G–screws to adjust D to the camera center, H–the tube to let the gas into the camera, I–the slit system, J–the film, K–the glass window through which the condensed gas on D is observed, L–the glass window through which the sample on D is illuminated by a small electrical lamp, M, N–tubes to vaccum pump.

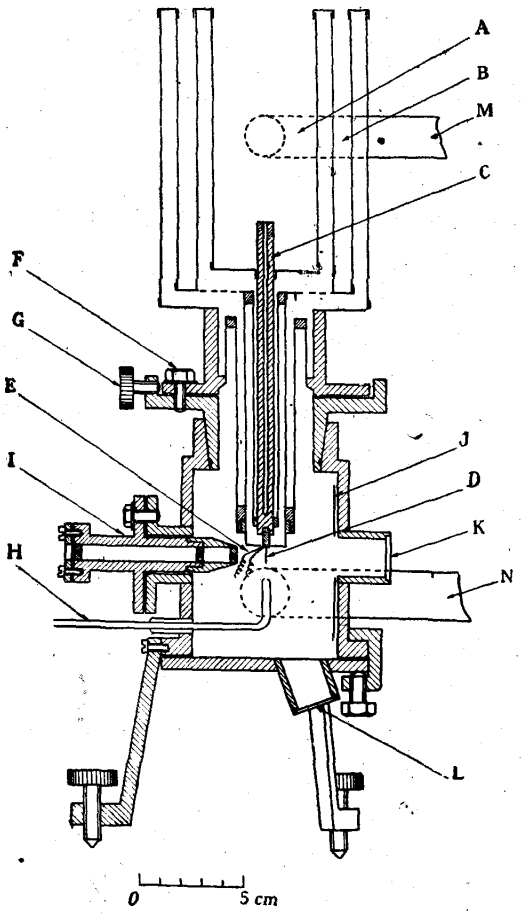

Fig. 1. Low temperature x-ray camera.

The experimental procedure was as follows. The Dewar's container and the camera itself were evacuated to high vacuum and then the cooling liquid was poured into the cryostat. When the temperature of the metal wire D had reached the desired point, the gaseous sample was introduced into the camera. The thickness of the crystal layer was controlled to be 0.1~0.2 mm so as to record the powder lines of the wire metal on the same film. Then the sample was subjected to x-ray irradiation. The metal wire (D) used in this experiment was of silver (99.99%), copper (99.9%) or platinum, its diameter was 0.5 or 0.7 mm. Two slit systems were employed, the one was about 60 mm. long and the other was about 200 mm. long. When the longer slit system was used, the incident x-ray beam became practically parallel and very fine powder lines were obtained. This fact was very advantageous in

(13) L. Vegard, Z. f. Phys., 58 (1929) 497.
(14) P. Günther, K. Holm and H. Struntz, Z. Phys Chem., B43 (1939), 229.

the case of the sulfur dioxide crystal.

X-rays from the copper anticathode were employed throughout this work, and K_β radiation was eliminated by the nickel filter.

III. Experimental Results

1. The photographs. With the camera described above several powder photographs of sulfur dioxide were obtained at the temperature of liquid air. Because of the thin layer of crystals, the powder lines of the metal wire were recorded on the same film, from which the camera constant was calculated. Some of the sulfur dioxide lines were overlapped on the metal lines accidentally. Therefore, photographs of the material deposited on different metals were compared to distinguish them. Sometimes, we recorded the carbon dioxide lines on the same film, from which we could calculate the camera constant with the lattice constant of carbon dioxide determined by Keesom[15].

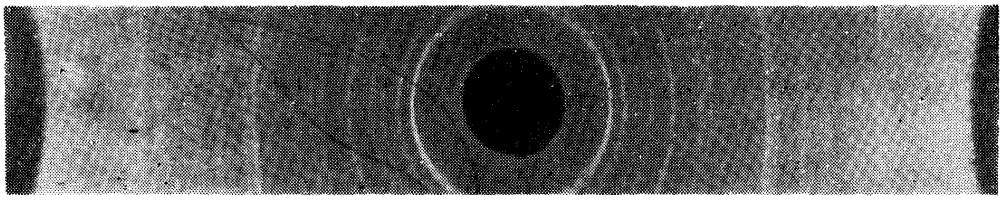

Fig. 2. Powder photograph of sulfur dioxide, Cu-K_α radiation, 95°K.

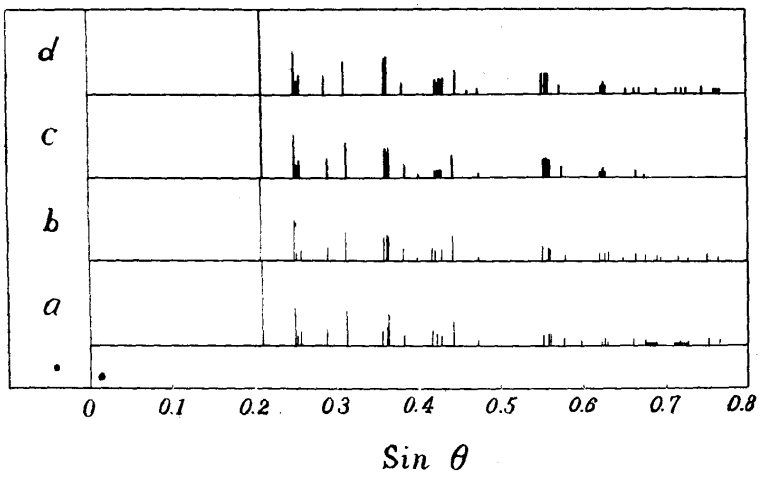

Fig. 3. Comparison of powder photographs.

2. Correction of the lines. Different correction formulas for powder lines of condensed gases were suggested by Keesom[16] and Simon[17]. But their formulas were not adequate for sulfur dioxide. While, Nishiyama[18] compared various correction formulas of the ordinary powder photograph with his observation, and proposed a rather complicated formula. In our case, as the linear absorption

(15) W.H. Keesom and J.W.L. Köhler, Comm. Leiden, No. 230b (1934), No. 232c (1934)
(16) J. de Smedt and W.H. Keesom, Comm. Leiden, No. 53a (1924).
(17) F. Simon and Cl. von Simon, Z. f. Phys., 21 (1924) 68.
(18) Z. Nishiyama, Sci. Rep. Tohoku Univ., 21 (1932), 364.

coefficient of sulfur dioxide for copper-K_α radiation is about 100, a correction formula of simple form for the substance of moderate absorption coefficient is desirable. After some trials, we have decided to apply Hadding's formula:

$$\Delta 2l_m = \rho\,(1 + \cos 2\theta)\ , \qquad (1)$$

where ρ is the radius of deposit, θ is the glancing angle and $\Delta 2l_m$ is the correction for the line center. The values of sin θ of the lines thus corrected and averaged over all photographs are illustrated in Table 1.

3. Intenstiy measurements. The relative intensity of the lines were measured by comparing with a series of standard spots which were exposed to monochromatic copper-K_α radiation of known intensity.

In the x-ray structure analysis of condensed gases, the absorption correction of the intensities has never been applied even for substances of relatively large absorption coefficient. But this correction must be applied to get quantitative results except for light molecules. Tables of the absorption correction for ordinary powder photographs were published by Classen[19] and Blake[20]. It is evident from Fig. 4 that these are not applicable in our case. Therefore we calculated the absorption correction for our experimental condition by using the method of Classen. The absorption factor A is the ratio of the intensity of the diffracted

Table 1. Powder lines of sulfur dioxide.

No.	sin θ (obs.)	sin θ (calc.)	hkl	I (obs. corr)
	0.2227	0.2216	111	560
2	0.2518	0.2530	002	127
3	0.2539	0.2553	200	25
4	0.2585	0.2590	020	35
5	0.2890	0.2888	120	47
6	0.3132	0.3129	211	68
7	0.3592	0.3593	202	34
8	0.3625	0.3621	022	66
9	0.3638	0.3637	220	
10	0.3828	0.3839	122	26
11	0.4192	0.4207	113	26
12	0.4226	0.4236	311	18
13	0.4284	0.4281	131	18
14	0.4431	0.4431	222	34
15	0.4746	0.4753	213	9.5
16	0.5548	0.5544	313	22
17	0.5582	0.5579	133	17
18	0.5602	0.5600	331	26
19	0.5712	0.5698	204, 024	8.5
20	0.5779	0.5725	402, 420	
		0.5776etc	042, 240	
21	0.6232	0.6231	224	8.2
22	0.6266	0.6259	422	8.7
23	0.6314	0.6306	242	8.8
24	0.6572	0.6580	115	4.5
25	0.6642	0.6634	511	6.8
		0.6645	333	
26	0.6724	0.6722	151	6
27	0.7175	0.7187	404	6
28	0.7274	0.7241	044	6
		0.7275	440	6

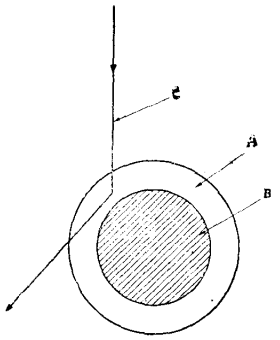

Fig. 4 Section of the specimen.
A: sulfur dioxide crystal,
B: metal,
C: path of x-rays.

(19) A. Claassen, Phil. Mag., (7) 9 (1930), 57.
(20) F. C. Blake, Rev. Mod. Phys., 5 (1933), 163.

beam to that of the incident and is given by the equation:

$$A = \sum e^{-\mu\rho x} \Delta s \ , \qquad (2)$$

where μ is the linear absorption coefficient and ρ is the radius of the specimen, Δs is the area of a strip, for which the path of the beam at a given glancing angle has a length between ρx and $\rho(x+\Delta x)$. To evaluate A, the region of the specimen effective for diffraction was divided into a number of strips and the summation was carried out numerically. The average values of the intensity of each line corrected for absorption are given in Table 1.

IV. Determination of crystal structure

1. **The unit cell.** The indexing of the powder lines was not easy. At first, Ito's method[5] was tried but failed, because the lines were too complicate and the accuracy of the experiment was insufficient for Ito's method.

Then Hull-Davey graphical method was applied to find the approximate lattice. For this trial, the photograph containing relatively few lines (Fig. 3c) was employed and broad lines on the photograph were regarded as single lines. Several cases belonging hexagonal, rhombohedral and tetragonal system were found satisfactory to explain all the lines. For each case, number of molecules Z in the unit cell was calculated using the value 1,928 for the density of sulfur dioxide crystal at $-191°C$[21]. The cases which gave nearly integral value of Z was that belonging to tetragonal system with c/a=1.02 or 0.98. Thus we concluded that sulfur dioxide crystallized in pseudo-cubic system. But some of the broad lines on the films which obtained with the long slit were splitted into two or three lines against these obtained with the short slit. The circumstance is well illustrated in Fig. 3. This was not explained by tetragonal system; for example, the lines of (200) type would be (200) and (002) in tegragonal system, while three lines were observed on the films. Therefore, sulfur dioxide did not belong to tetragonal but orthorhombic system. After some trials, the best values of the unit cell dimensions explaining the observation well were determined as follows:

$$a = 6.03\text{Å} \ ,$$
$$b = 5.94\text{Å} \ ,$$
$$c = 6.08\text{Å} \ .$$

Hear, a-, b- and c-axis are mutually interchangable. The number of molecules in the unit cell was:

$$Z = 3.95 \sim 4 \ .$$

Assuming Z=4, the calculated density at 95°K was 1.94, while the Biltz's value was 1.928 at $-191°C$[21].

For this choice of the unit cell the agreement of the values of the calculated $\sin\theta$ with the observed was satisfactory as was shown in Table 1.

2. **The space group.** All the reflections were missing except for (hkl) k+l= even, for (hko) k=even, for (okl) k=even and l=even, for (hol) h=even and l=even, for (hoo) h=even, for (oko) k=even, and for (ool) l=even. For these

(21) W. Biltz and O. Hülsmann, Z. Anorg. Chem., 207 (1932), 377.

conditions, the characteristic space groups should be.

$$D_{2h}^{18},\ C_{2v}^{17};$$

and the possible space groups should be

D_{2h}^{1}, D_{2h}^{3}, D_{2h}^{4}, D_{2h}^{5}, D_{2h}^{6}, D_{2h}^{7}, D_{2h}^{8}, D_{2h}^{9}, D_{2h}^{10}, D_{2h}^{11}, D_{2h}^{12}, D_{2h}^{13}, D_{2h}^{14},
D_{2h}^{15}, D_{2h}^{16}, D_{2h}^{17}, D_{2h}^{18}, D_{2h}^{19}, D_{2h}^{21},
D_{2}^{1}, D_{2}^{2}, D_{2}^{3}, D_{2}^{4}, D_{2}^{5}, D_{2}^{6},
$C_{2v}^{1}(a, b, c)$, $C_{2v}^{2}(a, b, c)$, $C_{2v}^{3}(b, c)$, $C_{2v}^{4}(a, b, c)$, $C_{2v}^{5}(a, b, c)$, $C_{2v}^{6}(b, c)$,
$C_{2v}^{7}(a, b, c)$, $C_{2v}^{8}(a, b)$, $C_{2v}^{9}(a, b)$, $C_{2v}^{10}(b)$, $C_{2v}^{11}(a)$, $C_{2v}^{12}(a)$, $C_{2v}^{14}(a, c)$,
$C_{2v}^{15}(b, c)$, $C_{2v}^{16}(b)$, $C_{2v}^{17}(b)$.

Also the observed reflections satisfied the condition: for (hkl) only k+l=even, for (hko) only k=even, for (okl) only k+l=even, and for (hol) only h and l=even. For this condition the characteristic space groups should be

$$D_{2h}^{17},\ C_{2v}^{12}(a),\ C_{2v}^{16}(c),$$

and the possible space groups should be

D_{2h}^{1}, D_{2h}^{4}, D_{2h}^{5}, D_{2h}^{6}, D_{2h}^{7}, D_{2v}^{9}, D_{2h}^{11}, D_{2h}^{12}, D_{2h}^{13}, D_{2h}^{14}, D_{2h}^{16}, D_{2h}^{17}, D_{2h}^{19},
D_{2}^{1}, D_{2}^{2}, D_{2}^{3}, D_{2}^{4}, D_{2}^{5}, D_{2}^{6},
$C_{2v}^{1}(a, b, c)$, $C_{2v}^{2}(a, b, c)$, $C_{2v}^{4}(a, c)$, $C_{2v}^{5}(a)$, $C_{2v}^{6}(b, c)$, $C_{2v}^{7}(a, b, c)$,
$C_{2v}^{8}(a)$, $C_{2v}^{9}(a, c)$, $C_{2v}^{10}(c)$, $C_{2v}^{11}(a)$, $C_{2v}^{12}(a)$, $C_{2v}^{14}(b, c)$, $C_{2v}^{16}(c)$.

Therefore, almost all the space groups of the orthorhombic system except for those derived from the face-centered or body-centered lattice were possible for either condition described above.

Since there had been no researches on the properties of crystalline sulfur dioxide which were closely related to the crystal structure, no further choice of space groups was made at this stage.

3. The atomic arrangement. The next step is the selection of the space groups and the atomic coordinates which explain the observed intensities. Here, the atomic coordinates must be examined over the whole volume of the unit cell for each of the possible space groups. But it involved very troublesome calculations and was impossible without any simplifications. Therefore, we made some assumptions to make the further analysis easy.

The assumptions were:

(a), sulfur dioxide crystallizes in molecular crystals;

(b), there are no molecular pairs such as proposed by Giauque, nor chain or net work of molecules;

(c), the atomic distances between neighboring molecules are equal to or larger than 3 Å;

(d), in surfur dioxide molecule, the S−O distance is equal to 1.43 Å and the angle <OSO equal to 120°±5°.

The assumption (a) is reasonable, because the molecular heat of sublimation of sulfur dioxide is 8.48 kcal and of ordinary amount among those of the other

molecular crystals[22], and there is no indication of molecular association in the liquid.

As cited in section I, Giauque[12] has proposed the existence of molecular pairs in the crystal to explain the abnormal thermal expansion near the melting point of sulfur dioxide. But this abnormality may be accounted for by another reason. Moreover, if there were any molecular pairs, the heat of sublimation would become somewhat larger, or in the liquids there would be some abnormalities in the surface tension etc., but these are not the case. Therefore, the assumption (b) is acceptable.

The van der Waal's radius of oxygen and sulfur are 1.40 Å and 1.85 Å respectively after Pauling[23]. These value is not unique and may be altered according to the state of atoms in the compounds. So in the assumption (c), the minimum of the atomic distances between neighboring molecules was assumed to be 3 Å.

The assumption (d) is based on the results of electron diffraction investigations on the molecular structure. Wierl[8] determined the S – O distance as 1.37 Å, Cross and Brockway[9] the S–O distance as 1.46±0.002 A and the angle <OSO as 124±15°, recently Schomaker and Stevenson[10] determined the S–O distance as 1.43 A and <OSO as 120±5°. In the assumption (d) the most reliable values of Schomaker's were taken. Thus all the above assumptions are reasonable and may be useful in the further analysis.

Then the 42 possible space groups* were examined and those which conflicted with the above assumptions were excluded.

At first, those which had at most four equivalent points were excluded, because all the atoms should occupy the general positions in those cases and we should determine 12 parameters at least. This selection involved certain arbitrariness but it was inevitable for the simplification of the analysis. The space groups thus excluded were:

C_{2v}^1, C_{2v}^2, C_{2v}^3, C_{2v}^4, C_{2v}^5, C_{2v}^6, C_{2v}^7, C_{2v}^8, C_{2v}^9, C_{2v}^{10},
D_2^1, D_2^2, D_2^3, D_2^4.

Of the remaining space groups, those where the neighboring molecules came to near in contradiction to the assumption (c) or (b) when we placed the atoms at its equivalent positions, were ommited. Those were:

C_{2v}^{11}, C_{2v}^{14}, C_{2v}^{15}, D_2^6, D_{2h}^1, D_{2h}^2, D_{2h}^3, D_{2h}^4, D_{2h}^5, D_{2h}^6, D_{2h}^9, D_{2h}^{10}, D_{2h}^{11}, D_{2h}^{13}, D_{2h}^{20}.

Moreover, the shape of the sulfur dioxide molecule became linear in some space groups in contradication to the assumption (d) when we placed the atoms at its equivalent positions. These space groups, i. e., D_{2h}^{15}, D_{2h}^{18}, D_{2h}^{21} were also excluded.

After these selections, the following space groups remained:

(22) c. f., Landolt-Börnstein-Roth-Scheel, Phy. Chem. Tabellen.
(23) L. Pauling, The Nature of the Chemical Bond, 2nd. ed., (1940), p. 189.
* By possible space groups, we meant here all the space groups of orthorhombic system except for these derived from the face-centered or body-centered orthorhombic lattice.

C_{2v}^{12}, C_{2v}^{16}, C_{2v}^{17},
D_2^5,
D_{2h}^7, D_{2h}^8, D_{2h}^{12}, D_{2h}^{14}, D_{2h}^{16}, D_{2h}^{17}, D_{2h}^{19}.

Here we must mention to the fact that the powder photograph of sulfur dioxide resembles to that of α-nitrogen[24] or α-carbon monoxide[25] with respect to the appearence of lines and their intensities. These crystals belong to the space group T^4, and the molecular centers take nearly the face center positions in the unit cubes. Therefore sulfur dioxide molecules or sulfur atoms may take the like positions.

Thus, the above 11 space groups and also C_{2v}^5, C_{2v}^9, D_2^4, which were at first excluded, were examined in detail. We placed four sulfur and eight oxygen atoms at all the possible positions satisfying the above assumptions and compared the calculated intensities of the typical reflections with the observation. The intensity was calculated according to the equation:

$$I\,(\text{calculated}) = I/A = \frac{1+\cos 2\theta}{\sin^2\theta\,\cos\theta}\cdot H\cdot F^2\cdot e^{-2M}, \qquad (3)$$

where $1+\cos 2\theta/\sin^2\theta\cdot\cos\theta$ is Lorentz-polarisation factor, A is the absorption factor, H is the so called *Flächenhäufigkeitsfaktor*, e^{-2M} is the temperature factor and F^2 is:

$$F^2 = A^2 + B^2,$$

where $A = \sum f \cos 2\pi\,(hx+ky+lz)$,

and $B = \sum f \sin 2\pi\,(hx+ky+lz)$*.

In general the temperature factor e^{-2M} cannot be determined theoretically. For ordinary crystals not so hard, it is well known that the exponent 2M takes the value 3×10^{-16} from experience. While, it can be calculated from Debye-Waller theory in the case of cubic monoatomic crystals. In the sulfur dioxide crystal, assuming the sulfur dioxide molecule as one atom placed at the face-center positions of cubic lattice, we obtained 2.2×10^{-16} for 2M using the characteristic temperature 120°K given by Giauque[11]. Considering the above, we decided to use the value $2M = 2.5\times10^{-16}$ for the approximate temperature factor.

Although the intensity calculations were very troublesome, we succeeded in determining the most probable space groups and the atomic coordinates. The space group was C_{2v}^{17} – Aba and the atomic positions were approximately:

4S: in(a), $(000)(0\frac{1}{2}\frac{1}{2})+$ $00z$; $\frac{1}{2}\frac{1}{2}z$ with $z_s = 0.00$;

8O: in(b), $(000)(0\frac{1}{2}\frac{1}{2})+$ xyz; $\bar{x}\bar{y}z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$
with $x_0\sim0.15$, $y_0\sim0.14$, $z_0\sim0.12$.

The next step was the more precise determination of these coordinates. From the intensities of (200) and (020) the difference of the parameters x_0 and y_0 were about 0.01. Retaining this relation and fixing the S–O distance at 1.43 A, the

(24) L. Vegard, Z. f. Phys., 58 (1929), 497.
(25) L. Vegard, Z. f. Phys., 61 (1930), 185.
* In the actual calculations, Lonsdale's forms for A and B were employed. K. Lonsdale, Structure Factor Tables, Bell and Sons, London, 1936.

Table 2. Comparison of the calculated intensities for various values of ∠OSO.

hkl	<OSO=110°		<OSO=120°		<OSO=130°		I (obs. corr.)
	F^2 (calc.)	I (calc.)	F^2 (calc.)	I (calc.)	F^2 (calc.)	I (calc.)	
111	4.43	598	4.24	573	4.20	567	560
002	3.80	102	4.78	129	5.75	154	127
200	1.25	33	0.94	24.5	0.72	19	25
020	1.79	45	1.33	33.2	1.17	28	35
120	1.18	44	1.23	46.6	1.28	48	47
211	0.90	53	0.95	57	1.01	60	68
202	1.74	37	1.51	33	1.45	31	34
022	1.63	} 68	1.60	} 70	1.45	} 70	} 66
220	1.64		1.78		1.90		
122	0.80	29	0.84	30.5	0.87	31	26
113	0.71	20	0.99	28	1.27	37	26
311	0.80	22	0.68	19	0.57	16	18
131	0.85	23	0.73	20	0.64	19	18
222	1.32	32	1.31	31.5	1.39	34	34
213	0.47	10	0.49	10	0.48	10	9.5
313	2.27	28	1.86	23	1.62	20	22
133	1.96	24	1.71	20	1.53	19	17
331	2.22	28	2.63	31	2.90	36	26

Table 3. Comparison of the calculated and the observed intensities*.

hkl	sin θ (obs.)	sin θ (calc.)	I (calc.)	I ** (obs. corr.)	hkl	sin θ (obs.)	sin θ (calc.)	I (calc.)	I ** (obs. corr.)
100	—	0.1277	0	0	331	0.5602	0.5600	31	26
011	—	0.1810	0	0	204		0.5666	10	8.5
111	0.2227	0.2216	573	560	024		0.5683	8.2	8.5
002	0.2518	0.2530	129	130	402	0.5712	0.5698	8	8.5
200	0.2539	0.2553	24.5	25	420		0.5726	7	8.5
020	0.2585	0.2590	33.2	35	042		0.5766	7	8.5
102	—	0.2833	0	0	240	0.5779	0.5776	8.5	8.5
120	0.2890	0.2888	46.6	47	124	—	0.5825	4.2	0
211	0.3132	0.3129	57	68	142	—	0.5906	0.6	0
202	0.3592	0.3593	33	34	233	—	0.6001	1.1	0
022	0 3625	0.3621	33	} 66	224	0.6232	0.6231	7.5	8.2
220	0.3638	0.3637	37		422	0.6266	0.6259	8 5	8.7
300	—	0.3830	0	0	242	0.6314	0.6306	8.5	8.8
122	0.3827	0.3839	30.5	26	340	—	0.6443	0.1	0
013	—	0.4009	0	0	015	—	0.6454	0	0
031	—	0.4087	0	0	304	—	0.6475	0	0
113	0.4192	0.4207	28	26	413	—	0.6491	0.8	0
311	0.4226	0.4236	19	18	051	—	0.6499	0	0
131	0.4284	0.4281	20	18	431	—	0.6540	0.3	0
222	0.4431	0.4431	31.5	34	115	0.6572	0.6580	4	4.7
302	—	0.4590	0	0	511	} 0.6642	0.6634	6.5	} 6.8
320	—	0.4624	0.8	0	333		0.6645	4	
213	0.4746	0.4753	10	9.5	151	0 6724	0 6722	5	6
231	—	0.4821	3.2	0	324	—	0.6853	1.1	0
004	—	0.5058	1.5	0	502	—	0.6866	0	0
400	—	0.5106	0.6	0	520	—	0.6888	1.2	0
040	—	0.5133	0.3	0	342	—	0.6921	0.1	0
104	—	0.5217	0	0	215	—	0.6932	1.3	0
322	—	0.5270	0.8	0	251	—	0.7067	1.9	0
140	—	0.5309	0.5	0	404	0.7175	0.7187	5.5	6.2
411	—	0.5417	2.0	0	044	} 0.7274	0.7241	6.3	6.2
033	—	0.5431	0	0	440		0.7275	5	6.2
313	0.5540	0.5544	23	22					
133	0.5582	0.5579	20	17					

* In the table, the reflections for which k+1 is odd were excluded, because these were not observed and the theoretical intensities must be zero from the requirments of the space group C_{2v}^{17}.

** I (obs. corr.) means I_{obs}/A, that is the observed intensity corrected for absorption.

angle <OSO was changed and the corresponding intensities were calculated. In Table 2 we illustrated a comparison of the calculated and observed intensities for each of the angles 110°, 120° and 130°. Of these, the most satisfactory agreement was obtained when <OSO was equal to 120°. Thus the final values of the atomic coordinates were determined as follows:.

4S : $z_s = 0.000$;

80 : $x_0 = 0.151$, $y_0 = 0.141$, $z_0 = 0.117$.

In Table 3 the calculated and the observed intensities were compared in detail for the final values of atomic coordinates.

4. The crystal structure. From the above analysis, the structure of sulfur dioxide crystal were determined as follows:

crystal system : orthorhombic;

unit cell : a=6.03 Å, b=5.94 Å, c=6.08 Å;

number of molecules per cell : z = 4;

space group : C_{2v}^{17} – Aba.

atomic coordinates : 4S, (000)$(0\frac{1}{2}\frac{1}{2})+$ 00z; $\frac{1}{2}\frac{1}{2}$z,

$z_s = 0.000$;

80, (000)$(0\frac{1}{2}\frac{1}{2})+$

xyz; $\bar{x}\bar{y}z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$,

$z_0=0.151$, $y_0=0.141$, $z_0=0.117$.

The atomic arrangements in a unit cell are illustrated in Fig. 5. This structure gives 1.43 Å for the S–O distance and 120±5° for <OSO in good agreement with the electron diffraction data.

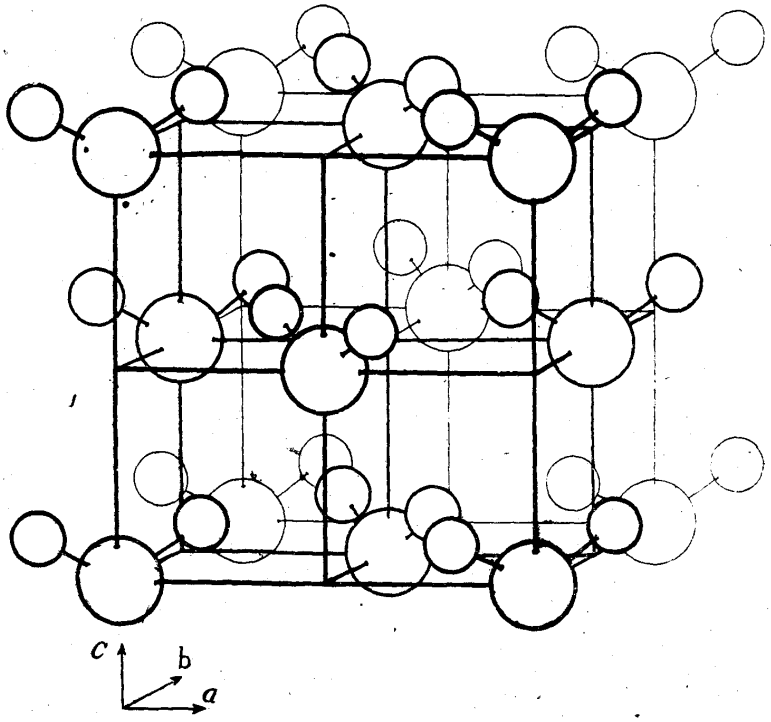

Fig. 5. Crystal structure of sulfur dioxide.
The large spheres: sulfur, small spheres: oxygen

The atomic distances between neighboring molecules in the crystal are shown in Table 4.

Table 4. Interatomic distances in sulfur dioxide crystal.

atom	neighboring atoms		distances	notes
	number	sort	(Å)	
S	4	S	4.24	
	4	S	4.26	
	4	S	4.29	
	2	O	1 43	S-O distance in the molecule.
	2	O	3.10	shortest distance between molecules.
	2	O	3.26	
	2	O	3.30	
O	1	S	1.43	O-S distance in the molecule.
	1	S	3.10	shortest distance between molecules.
	1	S	3.26	
	1	S	3.30	
	1	S	4.39	
	1	S	4.42	
	1	O	2.49	O-O distance in the molecule.
	2	O	3.22	
	4	O	3.28	
	2	O	3.77	

V. Discussion

1. On the method of analysis. In the indexing of the powder lines we employed the graphical methods of Hull and Davey. This leaves the results of the analysis somewhat arbitrary especially for wide angle reflections. But fortunately, sulfur dioxide had pseudo-cubic lattice, the indexing was relatively easy. The agreements between the calculated and observed values of $\sin\theta$ and intensities showed that our choice of the lattice was adeqate.

In the determination of atomic coordinates, it was inevitable to use some assumptions to make the calculations easy. As described in the previous section, our assumptions were quite reasonable. Moreover the resulting structure did not conflict with these assumptions. From these points, our method of the structure determination was not inadequate.

Sometimes the powder method of crystal analysis leads to a false conclusion. As an example, two different structures of nitrogen dioxide crystal giving good agreements between the calculated and observed intensities were proposed by Hendricks[26] and Vegard[27]. The structure given by Hendricks was more probable than that of Vegard, for the former was determined so as to be consistent with the molecular structure obtained by the infra-red spectra.

In general, when the obtained crystal structure are consistent with the physical and chemical properties of the crystal or the molecular structure of the component molecule, the structure may be regarded true one even if the determination was carried out by powder photographs only. Therefore, in our case, the crystal structure of sulfur dioxide must be examined from the stand point of physical and chemical properties.

(26) S. B. Hendricks, Z. f. Phys., 70 (1931), 699.
(27) L. Vegard, Z. f. Phys 68 (1931), 184; ibid., 71 (1931), 299

2. On the crystal structure. It is interesting that all the molecules orientate in one direction (c-axis) in the crystal of sulfur dioxide. The dipole moment of this molecule is 1.60 Debye unit., so the crystal must have marked polar characters. For example, the crystal must have electric moment along c-axis. Moreover the thermal conductivity and the thermal expansion will show anomalous values along this axis. But measurements of these properties have not been published, we can not discuss on this point.

When the molecules with large dipole moments are arranged parallel in a crystal, the interaction energy of these dipoles will contribute considerably to the cohesive energy of the crystal. As described in the previous section the dipoles are located in the face-centered positions of the pseudo-cubic cell in the crystal of sulfur dioxide, so that the parallel arrangement has negative and deeper interaction energy than any other from the theory of dipole interaction in crystals[28]. This is a quite qualitative argument and it is needed to calculate the lattice energy of the crystal and to compare it with the observation for the further confirmation of the structure determined here.

In connection with this fact, the abnormal thermal expansion of sulfur dioxide crystal near the melting point may be explained as follows: the molecules are combined relatively tight by the dipole-dipole interactions, and near the melting point the large expansion of the crystal may be necessary to release the combinations between molecules.

Another example of the crystal having parallel dipole arrangements is carbonyl sulfide COS, whose structure has been determined by the same methods as used in this paper[29]. In this crystal the COS molecules make molecular chains and in the chain the S−O distance between neighboring molecules are about 3 A.

The interatomic distances between neighboring molecules are somewhat smaller than the corresponding distances in the other molecular crystals. This contraction would be caused by the above mentioned dipole-dipole interaction in the sulfur dioxide crystal.

The shape of the molecule determined by electron diffraction methods is maintained in the crystal, and this fact favors our structure.

Concluding Remarks.

The authors express their thanks to Mr. Umejiro Yoshida, Mr. Junichi Nagasaki the late research engineers of Nippon Denki Kaisha, and also the staffs of the company for their helps to construct the low temperature x-ray camera in the time of want during the latest war. The authors also wish to thank the members of the "Research Institute of Scientific Measurement" for their skillfullness to make this apparatus.

One of the authors, Tadashi Sugawara with to thank his wife Ruriko Sugawara for her help in the laborious calculations throughout this work.

In conclusion, this work has been aided by a fund from the Scientific Research Expenditure of the Department of Education.

(28) J. A. Sauer, Phys. Rev., 57 (1939), 142.
J. M. Luttinger and L. Tisza, Phys. Rev., 70 (1946), 954.
(29) L. Vegard, Z. Krist., 77 (1931), 411.